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Attorney Docket No.: NSL-025

PATENT APPLICATION
HIGH THROUGHPUT SURFACE TREATMENT ON COILED
FLEXIBLE SUBSTRATES

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Filed: February 19, 2004

Express Mail Label Number: EF084591344US

HIGH THROUGHPUT SURFACE TREATMENT ON COILED FLEXIBLE SUBSTRATES

CROSS-REFERENCE TO RELATED APPLICATION

This application is related to commonly-assigned co-pending application serial no. _____, titled "DEVICE BASED ON COATED NANOPOROUS STRUCTURE" (Attorney Docket NSL-024), which is filed the same day as the present application, the entire disclosures of which are incorporated herein by reference. This application is also related to commonly-assigned, co-pending application serial no. _____, titled "ROLL-TO-ROLL ATOMIC LAYER DEPOSITION METHOD AND SYSTEM" (Attorney Docket No. NSL-026), which is filed the same day as the present application, the entire disclosures of which are incorporated herein by reference. This application is also related to commonly-assigned co-pending application serial no. _____, titled "SOLUTION-BASED FABRICATION OF PHOTOVOLTAIC CELL" (Attorney Docket NSL-029), which is filed the same day as the present application, the entire disclosures of which are incorporated herein by reference.

FIELD OF THE INVENTION

The present invention is directed to the deposition and/or surface treatment of thin films on large area substrates and more specifically to atomic layer deposition in a high-throughput production system.

BACKGROUND OF THE INVENTION

Several forms of surface chemistry and surface treatment depend upon the interaction of a substrate with its environment, including annealing, drying, and exposure to reactive gas. For example, Atomic Layer Deposition (ALD) is a high-quality thin-film deposition technique based on sequential, self-limiting surface reactions. Atomic layer deposition works by exposing a substrate sequentially to two or more reactant vapors or solutions and maintaining the substrate temperature within, for example, a temperature range that depends on the chemistry of the particular ALD reaction. A typical ALD process involves a sequence of two different and alternating surface reactions involving two different gaseous reactants referred to herein as A and B. The ALD system is typically purged of reactant gas in between reactions with a non-reactive purge gas C, and/or is pumped clean of the reactant gases. Sequencing the reactions provides precision in the rate of deposition and allows the use of highly reactive reactants. With each reactant exposure, a self-limiting reaction occurs on the

surface of the substrate if the substrate temperature is, for example, within the right temperature range, or alternative energy sources are provided, such as energetic ions or molecules or atoms, ozone, plasma, UV light, etc.

5 ALD can control the thickness of deposited films at the level of an atomic or sub-atomic layer. Thus films deposited by ALD tend to be uniform over large areas. In addition ALD allows deposition of conformal films on structures having very high aspect ratios (e.g., >> 10). A wide variety of materials may be deposited by ALD, including semiconductors, metals, oxides, nitrides, and other materials. ALD techniques can thus deposit thin films one atomic layer at a time, in a "digital" fashion. Such "digital" build-up of material greatly
10 simplifies thickness control, thus reducing both the complexity and cost of thin film deposition.

Many industries, such as the optoelectronics industry, can benefit from the high uniformity, high aspect ratio conformal coating abilities and low cost of ALD. Unfortunately, prior art ALD systems have mostly been made for semiconductor wafer processing, which is oriented
15 to batch processed wafer handling systems. Although existing ALD systems are suitable for the semiconductor industry, they are unsuitable for high volume manufacturing of large area devices such as photovoltaic cells. Current systems are typically designed to coat small area wafers. Scaling up systems that coat a small area at a time might not be practical for coating large area sheets, panels or rolls of material. ALD may be too slow and expensive overall, if
20 only small area batch processing can be performed. Further, surface treatments such as annealing, drying, and exposure to reactive gases cannot be carried out at high-volume for large-area substrates when the surface treatments and/or reactions take place in a relatively smaller treatment chamber.

Thus, there is a need in the art, for a high throughput surface treatment method and system.

25

BRIEF DESCRIPTION OF THE DRAWINGS

The teachings of the present invention can be readily understood by considering the following detailed description in conjunction with the accompanying drawings, in which:

FIG. 1A is a 3-dimensional exploded view schematic diagram of a high throughput atomic layer deposition system according to an embodiment of the present invention.

FIG. 1B is a 3-dimensional view schematic diagram of an alternative spindle for winding a substrate according to an embodiment of the present invention.

FIGs. 2A-2H are a sequence of schematic diagrams illustrating coiling of a substrate according to an embodiment of the present invention.

- 5 FIG. 3A is a three-dimensional schematic diagram of a spacer that may be used in a coiling a substrate an embodiment of the present invention.

FIG. 3B is an end view elevation of a stack of spacers of the type shown in FIG. 3A.

FIG. 3C is a three-dimensional schematic diagram of an alternative spacer that may be used in a coiling a substrate an embodiment of the present invention.

- 10 FIG. 3D is an end view elevation of a stack of spacers of the type shown in FIG. 3C.

FIG. 4 is a three dimensional schematic diagram of an alternative substrate carousel according to an embodiment of the present invention.

FIGs. 5A-5F illustrate the use of spacer tapes according to embodiments of the present invention.

- 15 FIGs. 6A is a cross-sectional schematic illustrating a substrate with spacer tapes wound on a spindle according to embodiments of the present invention.

FIG. 6B is a perspective schematic diagram illustrating multiple substrates wound side-by-side on a spindle according to an embodiment of the present invention.

FIG. 6C is a cross-sectional schematic diagram taken along line C-C of FIG. 6B.

20 DESCRIPTION OF THE SPECIFIC EMBODIMENTS

Although the following detailed description contains many specific details for the purposes of illustration, anyone of ordinary skill in the art will appreciate that many variations and alterations to the following details are within the scope of the invention. Accordingly, the exemplary embodiments of the invention described below are set forth without any loss of
25 generality to, and without imposing limitations upon, the claimed invention.

The inventors recognized that in atomic layer deposition systems, wherever the reactant gases A, B come in contact with substrate, good coating may be achieved. Consequently, ALD

may be readily scaled to coating large substrate areas in each reaction step. Thus, the throughput of an ALD system may be increased by massively scaling the substrate surface area processed during each step (as opposed to scaling up the step speed for each deposition cycle and/or processing many substrates in parallel via, e.g. the number of ALD reaction chambers) This can be achieved by coiling a flexible substrate (e.g., metal or alloy foil, e.g. Al, metalized plastic foil, otherwise coated foils, foils with pre-deposited/processed surface structure and/or patterning, laminates, etc.) in an ALD chamber in such a way that adjacent 'turns or windings' of the foil on the carrier roll, cassette, or carousel do not touch one another. Gaps between adjacent layers of the coiled substrate allow the reactant gases to flow or diffuse into the gaps between adjacent turns and thus reach and be adsorbed or react on the substrate surface(s) to be coated. Each step (A, B, C) of the ALD reaction may then be applied to a massive surface area of the substrate. The basic concept behind the embodiments of present invention is not so much a roll-to-roll implementation (in terms of continuous throughput) but one in which each step may be applied to the entire surface area of the substrate, e.g., in an entire roll. The same approach, with appropriate modifications, can be used to scale up other surface treatment techniques such as substrate annealing, drying, anodization, electro-deposition, electro-polymerization, electro-polishing, cleaning, exposing to chemicals to treat the surface (e.g. selenization of a substrate using H_2Se gas or Se vapor), solution treatments, treatments that require electric fields/current/voltage, etc.

One way to achieve high-volume production in ALD systems of the type described herein is to perform an ALD reaction on an entire roll of substrate material at one time. To do this, it would be useful to fit the entire length of a roll into the ALD chamber so that the A and B half-reactions can be performed without having to remove the substrate from the chamber. In another alternative embodiment, an entire roll of substrate material may be treated at one time by using a system of the type depicted in FIG. 1A. The system **100** includes a surface treatment chamber **102** and a carousel **104** for coiling a flexible substrate **106** in a way that allows gaps between adjacent turns of the coil. Gas sources **108**, **110** and **112** provide ALD reactants A, B and purge gas C to the chamber **102**. One or more robots **114** place stackable spacers **116** on the carousel **104**. An exhaust system **111** removes gas or liquid from within the chamber **102**. The gas pressure within the chamber **102** may be adjusted by appropriate control of the gas sources **108**, **110** and **112** and the exhaust system **111**.

By way of example, the chamber 102 may include an inner wall 103 and an outer wall 105. The substrate 106 may be wound outside the chamber 102 on the carousel 104, which fits between the inner wall 103 and the outer wall 105. The carousel 104 may be loaded into the chamber 102 through the top (or side). A lid 107 seals the top of the chamber 102. By way of example, the chamber 102 may also include equipment for pre-treatment of the substrate 106 by plasma, UV-ozone, heat (e.g., infrared), corona or combinations thereof. In addition, the chamber 102 may include equipment for performing one or more treatment and/or coating steps that are performed prior or subsequent to atomic layer deposition that is performed in the chamber 102, including but not limited to substrate cleaning, annealing, drying, and/or exposure to reactive gas such as Se vapor or H₂Se. Such post-ALD steps may include passivation, or coating the ALD treated substrate 106 with, e.g., an organic or inorganic material. In addition, the chamber 102 may be equipped with additional gas low inlets, heaters (e.g., infrared heaters, light sources, or ultraviolet radiation sources, sources for energetic particles such as plasma ions, ozone, etc.) or cooling mechanisms, such as fluid filled tubes or peltier effect (thermoelectric) elements. Furthermore, the chamber 102 may be part of a much larger coating line that may include other equipment for performing pre-ALD and post-ALD treatment of the substrate 106. The wound substrate can also be surface-treated in the absence of ALD processes, e.g. by carrying out substrate cleaning, and/or annealing, and/or drying, and/or exposure to reactive gas (such as Se vapor or H₂Se) in the absence of ALD. Further, the wound substrate can also be surface-treated in the absence of ALD processes, e.g. by carrying out anodization, electrodeposition, electroplating, electropolishing, and/or other reactions in the absence of ALD.

The carousel 104 may be regarded as a winding drum for the substrate 106, e.g., a foil, such as aluminum foil or another flexible foil such as a plastic or metallized plastic foil. The carousel 104 generally has a number of anchor points for the stackable spacers 116. By way of example, the carousel 104 is depicted as having a hexagonal cylindrical geometry with anchor points located at the edges of a hexagonal cylinder. By way of example, the carousel 104 may be made of six solid plates e.g. of stainless steel, connected into a hexagonal cylinder. Alternatively, the carousel 104 may be made of structural beams (e.g., steel or aluminum tubing or rods) that form an open frame in the shape of a hexagonal cylinder. In addition, the anchor points may stack onto a basic "core" hexagonal cylinder such that the entire structure may be allowed to expand or contract with changes in temperature. Although a hexagonal carousel 104 with six edges is described herein, the carousel 104 may have fewer

edges (e.g., 3, 4 or 5 edges) or more edges (e.g., 7, 8 or more) for locating the spacers **116**. Alternatively, a round carousel, drum, spindle, or roll may be used. For a carousel of a given diameter, the more anchor points there are the shorter the distance between anchor points and, thus, the less bending stress per contact point there will be on the substrate **106**. FIG. 1A shows the spacers **116** as rods along the entire width of the web, connected to locating/fixing points at both ends of the carousel. Alternatively as shown in FIG. 1B, spacers **116'** could be fixed at the sides of the substrate **106** only, protruding only partly into the carousel **104** and thereby holding the foil only at the sides, via pressure between adjacent spacers and/or stress on the foil as it is wound. The shorter spacers **116'** could, for example, have the shapes as shown in FIGs. 3A – 3D. Alternatively, these spacers could be round rods or round wheels at the sides of the substrate **106**. Alternatively, the spacer 'rolls/rods' could be knurled.

The carousel **104** and/or surrounding chamber may include an optional substrate temperature control element (e.g., heating and/or cooling element) to maintain the temperature of the substrate **104** within a specified range.

Gas sources **108**, **110**, supply reactant gases **A** and **B** for sequential atomic layer deposition processes that occur in the chamber **102**. Gas source **112** may supply an optional non-reactive purge gas **C**, e.g., an inert gas such as argon or argon. Alternatively, or in addition, reactant gases **A** and **B** (or better reactant gases **A** and **B** each mixed into a carrier gas such as nitrogen (N_2) or argon) could be removed via pumping. The gas sources **110**, **112**, **116** may selectively supply either reactant gas **A** or reactant gas **B** and/or purge gas **C** though one or more gas lines and one or more valves **113**. As described above, a temperature control element may be disposed in the chamber **102** or on the carousel **104** to control the temperature of the substrate **106** and/or chamber **102**. Alternatively or in addition, other energy sources could be used, such as energetic particles (from plasma, Ozone, etc.), UV light, etc. At the right range of temperature and/or presence of other energetic species and pressure each reactant gas **A**, **B** may participate in a half-reaction at the surface of the substrate **106**. When the two half-reactions are performed sequentially a very thin layer of material, e.g., as little as one atomic layer or (more common) part of one monolayer, may be deposited on the substrate **106** as a result of the two half-reactions. By way of example, where reagent **A** is $TiCl_4$ and reagent **B** is water vapor (H_2O), the two half-reactions deposit a layer of titania (TiO_2). Repetition of both half-reactions with appropriate purge/pump cycles in between creates thicker films deposited with high conformality and atomic layer precision.

Atomic layer deposition using these reactants is described, e.g., by M. A. Cameron, et al., in "Atomic Layer Deposition of SiO₂ and TiO₂ in Alumina Tubular Membranes: Pore Reduction and Effect of Surface Species on Gas Transport," *Langmuir* **2000**, 16, 7425-7444, American Chemical Society, Washington D.C., the disclosures of which are incorporated
5 herein by reference.

The coiling of the substrate **106** may proceed as depicted in FIGs 2A-2H. The substrate may be wound onto a conventional roll **118**. A portion of the substrate **106** may be unwrapped from the roll **118** and attached to the carousel **104**. Spacers **116** may be placed at predetermined locations on the carousel **104**. As the carousel **104** turns, the substrate **106**
10 unwinds from the roll **118** and passes over the spacers **116** as shown in FIG. 2A. Alternatively, the roll **118** may be moved circumferentially about the carousel **104** as the substrate **106** unwinds from the roll and is coiled about the carousel **104**. It is also possible to coil the substrate by some combination of rotation of the carousel **104** and circumferential movement of the roll around the carousel **104** as the substrate **106** unwinds from the drum
15 **118**. Before a full turn (not necessarily the first turn) of the substrate **106** has been coiled around the carousel **104**, the robots **114** stack more spacers **116** on those that were initially on the carousel **104** as shown in FIGs 2B-2D. As the carousel **104** continues to rotate, the substrate **106** continues to unwind from the roll **118** and coil around the carousel **104**. A second "turn" of the coiled substrate **106** passes over the spacers **116** as shown in FIGs 2E-
20 2H. In the example depicted in FIGs. 2A-2H each spacer **116** touches a back surface of the substrate **106** but not a front surface of the substrate **106**, thus allowing treatment of substantially all of the front surface of the substrate **106**. If the spacers **116** are sufficiently close together, adjacent turns of the coiled substrate **106** may be prevented from touching each other without the need for excessive tension on the substrate **106**. The spacing depends
25 partly on the thickness of the substrate **106**, partly on the choice of substrate material and partly on the requirements of gas / reactant gas flow and the speed thereof into and out of the areas between foil windings. Tensioning devices may be incorporated into the winding mechanism so that the substrate **106** wraps around the carousel **104** with sufficient tension to keep adjacent turns of the substrate from touching one another. Note, with spacers just
30 mounted on the side, the issue of 'touching' does not arise.

Some high-volume batch processes, e.g., chemical bath deposition (CBD) and atomic layer deposition (ALD), could potentially coat or otherwise treat both sides of the coiled substrate

106 at one time. However, it may be desirable to coat only one side of the substrate 106. Coating or otherwise treating both sides can result in waste of valuable reactants or may lead to extra processing steps such as removing unwanted coatings. To avoid such waste or undesired processing, two substrates may be attached together "back-to-back" to form a dual
5 substrate having, in effect, two front sides with the back sides protected against undesired treatment. Preferably, the substrates are attached in a manner that allows them to be separated from each other after processing. By way of example the substrates may be attached with a low-strength adhesive or electrostatic film applied to the back side of one or both substrates. Alternatively, an edge where the two substrates join may be sealed, e.g.,
10 with a tape, so that reactants cannot reach the back sides during processing. The dual substrate may then be wound into a coil and coated such that both front surfaces are treated while the back surfaces are not. Processing the substrate in this fashion may reduce the waste of reactants and may increase the area of the substrate that can be processed at one time.

In order to provide sufficient spacing and tension in the substrate 106, several different
15 designs for the spacers 116 may be used. For example, FIGs. 3A-3B depict a spacer 302 having a "stick" type design that may be attached at the edges of a carousel such as the carousel 104 depicted in FIG. 1 and FIGs. 2A-2H. The spacer 302 may include a thin elongated curved plate 304. The curve of the plate 304 may be designed for a specific geometry of the carousel (e.g. a 120° curve for a hexagonal carousel as in FIG. 1). Such a
20 design may advantageously provide smooth contact with the substrate, i.e., without high-pressure contact points. In addition, the shape of the curved plate 304 may provide better strength against bending of the spacer 302. The curved plate 304 can also be made quite thin. Multiple spacers 302 may be stacked on top of one another to facilitate coiling, e.g., as depicted in FIG. 2. By way of example, stacking buttons 306 may be placed near the ends of
25 the curved plate 304. The buttons 306 may snap fit into buttons (holes / recesses) on adjacent spacers so that two or more curved plates 304 may stack, e.g., as depicted in FIG. 3B.

An alternative scheme for stacking spacers is depicted in FIGs. 3C-3D. In this example, a spacer 312 may include a curved plate 314 with a mounting flange 315 attached at each end. Two or more stacking buttons 316 may be attached to each mounting flange 315 so that the
30 curved plate 314 may be supported in a way that is more resistant to twisting. Care needs to be taken to provide spacers with sufficient mechanical stability along the desired width of the web to be able to keep the foil-to-foil separation small (so as to maximize throughput) yet still ensure that the front and back-sides of the substrate 106 do not touch each other.

Other alternative spacer designs are also possible. For example, instead of just a "stick" like spacer, one can also have a 2 dimensional spacer that may support the entire width of the substrate in a structural or solid way. Such a flat-area coil guide may help keeping the foils from touching each other, etc.

- 5 In alternative embodiments of the invention, two or more substrates may be coiled side-by-side on the same carousel, e.g., to increase the total throughput of a system such as that shown in FIG. 1. For example, FIG. 4 depicts three substrates **406A**, **406B**, and **406C** wound around a carousel **404**. Each substrate may be wound on the carousel **404** as described above with respect to FIGs. 2A-2H. The substrates **406A**, **406B**, and **406C** may be wound
10 sequentially or wound simultaneously. They may also be wound separately and then be mounted on a central carrier carousel / spindle. Alternatively, the spacers in FIG. 4 could be placed less than the entire width of the webs **206 A - C**, but rather hold the foil only from the sides, e.g., as shown in FIG. 1B.

- In another embodiment, spacers can be connected to each other such that the front-side of the
15 substrate **106** is all connected to one power supply terminal via the spacers and the back-side (e.g. via an electrically insulated back-side coating on **106** or an electrically insulated inserted / laminated foil/mesh) of the substrate **106**, also via the spacers, whereby the spacers are set up such that one set connects the front sides and another the back sides of the substrate **106**. This embodiment can be useful for e.g. a wound-coil-based anodization process that relies on
20 an electro-chemical cell.

- In another embodiment of the invention, 'spacers' that allow the winding of the substrate **106** onto a carousel (or drum, spindle, roll, etc.) could be 'continuous'. For example, FIG. 5A illustrates a scheme in which a substrate **506** is rolled into a roll onto a spindle **504** and, as the substrate **506**, e.g., a foil or other flexible material, is rolled onto the roll, 'spacer tapes' **520**
25 are inserted at the two edges (or alternatively at multiple points along the width of the web; e.g. every few inches, every foot, etc.). The spacer tapes **520** provide contact and grip to the substrate **506** on both sides, assures that the front-sides of the substrate **506** do not touch the back-sides, together with sufficient tension during the winding process. The spacer tape **520** is 'porous' in the sense that gas and/or liquid can flow through the porous material
30 comprising the spacer 'tape' for e.g. the ALD process. This embodiment has the advantage of a continuous contact with the substrate **106** along its entire length, thus, for example, reducing the risk of high pressure/stress points. The spacer tape **520** may be of plastic, a

rubber, a foam, metal, composite materials, etc. as long as there are openings of sufficient number and cross section along its side to allow for efficient flow of gases or liquids in and out.

- 5 The spacer tapes 520 may be characterized by a width A and a thickness B. The openings in the spacer tape 520 may run substantially parallel to the width A. By way of example, the width A may range from a few millimeters to a few centimeters to tens of centimeters, preferably in the range of a few mm to a few cm. By way of example, the thickness B could be in the range of less than about 1 mm to greater than 1 cm, preferably less than about 5 mm thick. Generally the spacer tape needs to be sufficiently open and gas- or liquid permeable to
- 10 allow for reasonable process times (e.g. ALD gas fill and pump or purge, ramp time to reach a proper temperature for annealing, etc.). Any such spacer tape should be sufficiently mechanically robust such that when wound up in between turns of the substrate 106, with whatever tension is necessary, the openings in the spacer tape are still substantially open (e.g., not squashed together in the case of e.g. an elastic or 'rubbery' spacer tape).
- 15 There are several ways of implementing the spacer tape 520. For example, FIG. 5B shows an example of a spacer tape 522 in the form of a strip of unitary material having regularly passages 524 formed therethrough. FIG. 5C shows an alternative example of a spacer tape 526 having a top strip 527, a bottom strip 529 and regularly spaced spacers 528 disposed between them. Gaps 529 between the spacers 528 allow gas to flow through the spacer tape
- 20 526. In one example, the spacer tape 526 could have electrically insulating spacers with the top and bottom strips 527, 529 being electrically conductive, e.g. metal tapes. This could be used, for example, in an entire roll-based anodization, electro-deposition, electro-polishing or similar process whereby one part or side of the spacer tape 526 provides electrical contact to one side of the substrate 506 (e.g. a top, coating, or treatment side) and the other to the
- 25 respective back side of the substrate 506. In this example, one could, for example, use as the substrate 506 a foil (e.g. Al) with an insulating coating or laminate on the back, followed by a conductive (counter-electrode) coating or laminate or mesh (e.g. Pt) at the back of the insulating layer. Here, the conducting top and bottom strips 527, 529 of the spacer tape 526 would make contact to the e.g. Al and Pt side such that a potential, via an outside power supply, can be maintained and e.g. an anodization process could be performed. Also here,
- 30 the spacer tape 526 would overlap in part with the to-be-treated foil 506 and partially overlap with connectors to connect to a power supply (or potentiostat etc.).

In another embodiment, shown in FIG. 5D, a spacer tape 530 could be a laminate of two 'corrugated' tapes 532, 534 with passages 533 between the corrugations. Alternatively, as shown in FIG. 5E, a spacer tape 535 may be a laminate of one corrugated tape 536 with a flat tape 538 with passages 537 defined by the corrugations. Materials of the tapes may be chosen such that they provide good contact and grip to the substrate 506, match thermal extinction coefficients to be able to maintain sufficient strain or stress on the substrate 506 and carousel to keep the substrate 506 in place, and are chemically compatible with all desired processes etc. In yet another embodiment, shown in FIG 5F, a spacer tape 540 could be of the form of a 'chain', akin to a bicycle chain whereby links 542 (e.g. small rolls/connectors, or flat or slightly bent parts) having through passages are pivotally connected together in a flexible and 'windable' fashion. By way of example, the links 542 may be coupled by hollow tubes 544 that allow gas or liquid to pass. Alternatively 'side parts' 546 of the links 542 may be open to let gas/liquid pass. The individual side parts 546 may also be solid pieces of plastic or metal with tubular holes at the ends for the links plus openings in the solid pieces for the gas/liquid.

Those of skill in the art will be able to devise spacer tapes in other forms of continuous tapes, bands, or chains with openings along the sides to let e.g. ALD gases through. Such tapes could be disposable tapes to be used once and then discarded or reusable tapes to be used many times.

FIGS. 6A-6C illustrate how substrates can be wound using spacer tapes according to embodiments of the present invention. For example, in the side cross-sectional diagram of FIG. 6A, a substrate 606 e.g. a foil, may be clamped to a central roll, drum, or spindle 602 (e.g., by a mechanical clamp or adhesive.) and then the substrate 606 is wound up with intermediate spacer tapes 620. Gases 610, e.g., ALD reactants or purge gases, enter the spaces between the turns of the substrate via openings 622 in the sides of the spacer tapes 620, e.g., as described above. Although FIG. 6A shows only two spacer tapes 620 at the ends of the substrate 606, more could be used, e.g. to provide support in case of a wider foil. In such a case, the central spacer tapes (not shown in figure 6A would create non-ALD-coated or non-treated areas on substrate 606 and this can be designed such that these non-treated / non-coated areas are those that don't need to be for the final product. For example, in a photovoltaic (PV) cell, parts of the foil that are used for e.g. series and/or parallel-wiring of

adjacent individual PV cells to e.g. a higher voltage PV module. Alternatively, the non-coated or non-treated areas could be areas reserved for later encapsulation.

In another embodiment depicted in FIG. 6B-6C, a main drum, roll, or spindle 632 could be used to wind/unwind several narrower substrates 606A, 606B, 606C side-by side. By way of example, 5 1-foot wide foils or rolls may be wound on an e.g. 6 foot wide spindle). Spacer tapes 630 may be located at the sides of each substrate. 606A, 606B, 606C. Thus, there would be additional areas (see arrows) for the ALD gas to enter/leave the central wound-up coating areas from both sides. By keeping the individual substrates 606A, 606B, 606C narrower there is less of a problem with stress and less likelihood that the front and back sides of substrates 606A, 606B, 606C will touch each other. In such an embodiment, the spindle 632 may be hollow and provided with slots 634 to facilitate the passage of gas.

In another embodiment, individual rolls/webs, e.g. 6", 1ft etc. wide could be wound up using various embodiments of the present invention (spacer rods along entire web width, spacers at web sides/edges; spacer tape, etc.) and multiple of said rolls could then be mounted on a larger central spindle, ready for transfer into a treatment chamber.

The advantages of the coiled substrate approach of the embodiments of the present invention may be illustrated by a numerical example. Consider a coiled substrate that can fit into 16'x16'x12' space. Assume that the coil has an inner diameter of 1 meter (e.g., for a hexagonal carousel, the distance from the center to an edge of a hexagon). Assume that the coil has an outer diameter of 3 meters and that the width of the coil is 2 meters and the carousel is a little wider, e.g., 2.4 meters wide. Each turn of the coiled substrate is 1 meter long between the edges of the hexagon initially and 3 meters long when fully wound. The average length of each turn of the coiled substrate is thus 6 sides X 2 m/side. If the substrate has a thickness of 0.025 mm and adjacent turns of the coiled substrate are 1 mm apart, then the coiled substrate would have about $2 \text{ m} / 1.025 \text{ mm} = \sim 2,000$ turns about the carousel. The total area of the coiled substrate would be $2,000 \times 2 \text{ m} \times 6 \times 2 \text{ m} = 48,000 \text{ m}^2$.

In this numerical example, suppose that a deposition requires 25 repetitions of the four step sequence ACBC, i.e., filling the chamber with reactant A, purge with inert gas C, fill with reactant B, purge with inert gas C. If each purge, pump or fill step takes 10 minutes, the throughput may be estimated as the total area divided by the total number of steps and the time per step, e.g., $48,000 \text{ m}^2 / 10 \text{ min/step} / 100 \text{ steps} = 48 \text{ m}^2/\text{min} > 500$ square feet per

minute. If the time for each step can be reduced to only 1 minute, the throughput may be increased to >5,000 square feet per minute.

5 In embodiments of the present invention, the scaling of the ALD process is geared towards surface area maximization, not necessarily process step speed, thus leaving enough time for each step. Consequently, pumping, purging and filling can be ensured to be high quality, thus minimizing loss of coating quality by intermixing gases, etc. Although the whole process may take a considerable period of time to complete, a vast surface area of substrate may be coated at one time. Furthermore, the same coil / coil process can be used for other surface treatment processes, e.g., anodization, that precede or follow the ALD process, thus
10 obviating the need for and cost of many wind/unwind steps. In addition, the same coil / coil process can be used for other surface treatment processes, e.g. heating, cooling, annealing, drying, exposure to reactive gas, etc., independent of any ALD process, providing a generalized means for high-throughput surface treatment of coiled flexible substrates.

15 While the above is a complete description of the preferred embodiment of the present invention, it is possible to use various alternatives, modifications and equivalents. Therefore, the scope of the present invention should be determined not with reference to the above description but should, instead, be determined with reference to the appended claims, along with their full scope of equivalents. The appended claims are not to be interpreted as including means-plus-function limitations, unless such a limitation is explicitly recited in a
20 given claim using the phrase "means for."

WHAT IS CLAIMED IS:

- 1 1. A method for treating a substrate surface, comprising the steps of:
2 coiling one or more substrates into one or more coils in such a way that adjacent
3 turns of the coils do not touch one another;
4 placing the one or more coiled substrates in a treatment chamber; and
5 in the treatment chamber, treating substantially an entire surface of the one or
6 more coiled substrates with a surface treatment process.
- 1 2. The method of claim 1 wherein the surface treatment process includes one or
2 more atomic layer deposition (ALD) reactions.
- 1 3. The method of claim 2 wherein the one or more ALD reactions include exposing
2 the surface of the coiled substrate to a reactant vapor of the type MCl_x , where M is
3 a metal and x is an integer from one to four.
- 1 4. The method of claim 3, wherein the one or more ALD reactions include exposing
2 the surface of the coiled substrate to water vapor.
- 1 5. The method of claim 3 wherein MCl_x is $TiCl_4$.
- 1 6. The method of claim 1 wherein the surface treatment process includes
2 anodization.
- 1 7. The method of claim 1 wherein the surface treatment process includes drying.
- 1 8. The method of claim 1 wherein the surface treatment process includes annealing.
- 1 9. The method of claim 1 wherein the surface treatment process includes exposure to
2 reactive gas or vapor.
- 1 10. The method of claim 9 wherein the exposure to reactive gas or vapor includes
2 selenization.
- 1 11. The method of claim 1 where the surface treatment includes anodization.
- 1 12. The method of claim 1 where the surface treatment includes electrodeposition.
- 1 13. The method of claim 1 where the surface treatment includes electropolishing.

- 1 14. The method of claim 1 wherein coiling the substrate includes attaching an end of a
2 roll of substrate material to a carousel, rotating the carousel while unrolling the
3 substrate material from the roll to coil the substrate around the carousel, and
4 placing one or more spacers between adjacent layers of the coiled substrate before
5 the carousel completes a turn.
- 1 15. The method of claim 14 wherein each spacer touches a back surface of the
2 substrate but not a front surface of the substrate.
- 1 16. The method of claim 14 wherein placing one or more spacers includes stacking
2 one or more spacers on top of one another.
- 1 17. The method of claim 1 wherein coiling the substrate includes attaching an end of a
2 roll of substrate material to a carousel, moving the roll of substrate material
3 around the carousel while unrolling the substrate material from the roll to coil the
4 substrate around the carousel, and placing spacers between adjacent layers of the
5 coiled substrate before the roll completes a turn about the carousel.
- 1 18. The method of claim 1 wherein the one or more substrates include two or more
2 substrates coiled side-by-side on a carousel.
- 1 19. The method of claim 1 wherein coiling one or more substrates into one or more
2 coils in such a way that adjacent turns of the coils do not touch one another
3 includes placing a spacer tape between adjacent turns of the substrate.
- 1 20. The method of claim 19 wherein the spacer tape is orientated substantially parallel
2 to a length of the substrate.
- 1 21. The method of claim 19 wherein the spacer tape includes one or more passages
2 running substantially along a width of the spacer tape.
- 1 22. The method of claim 1 wherein coiling one or more substrates includes attaching
2 two substrates together back-to-back to form a dual substrate and coiling the dual
3 substrate.
- 1 23. The method of claim 22, further comprising separating the two substrates after
2 they have been treated in the treatment chamber.

- 1 24. A substrate surface treatment system, comprising:
2 a surface treatment chamber;
3 a carousel adapted to receive a flexible substrate material as a coil, the carousel
4 being sized to be received within the chamber with the substrate material coiled
5 around the carousel in one or more turns;
6 a winding mechanism configured to coil the substrate material about the carousel
7 to form a coiled substrate; and
8 one or more spacers, the spacers being configured to space apart adjacent turns of
9 the coiled substrate in such a way that the adjacent turns of the coiled substrate do
10 not touch one another; and
11 a mechanism adapted to place one or more of the spacers between adjacent layers
12 of the coiled substrate before the winding mechanism winds a full turn of the
13 substrate material about the carousel.
- 1 25. The system of claim 22, further comprising one or more sources of reactant gas
2 coupled to the chamber, the reactant gas being of a type suitable for performing
3 atomic layer deposition.
- 1 26. The system of claim 22, wherein the chamber is an anodization chamber.
- 1 27. The system of claim 22, wherein the carousel is in the shape of a polygonal
2 cylinder.
- 1 28. The system of claim 25 wherein the carousel is in the shape of a hexagonal
2 cylinder.
- 1 29. The system of claim 22 wherein the spacers can be secured in place with respect
2 to the carousel.
- 1 30. The system of claim 22 wherein the spacers can stack on top of one another.
- 1 31. The system of claim 22, wherein the spacers include one or more spacer tapes.
- 1 32. The system of claim 29 wherein the spacer tapes run substantially parallel to a
2 length of the substrate.

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- 1 33. The system of claim 29 wherein at least one spacer tapes is located proximate a
- 2 side of the substrate.

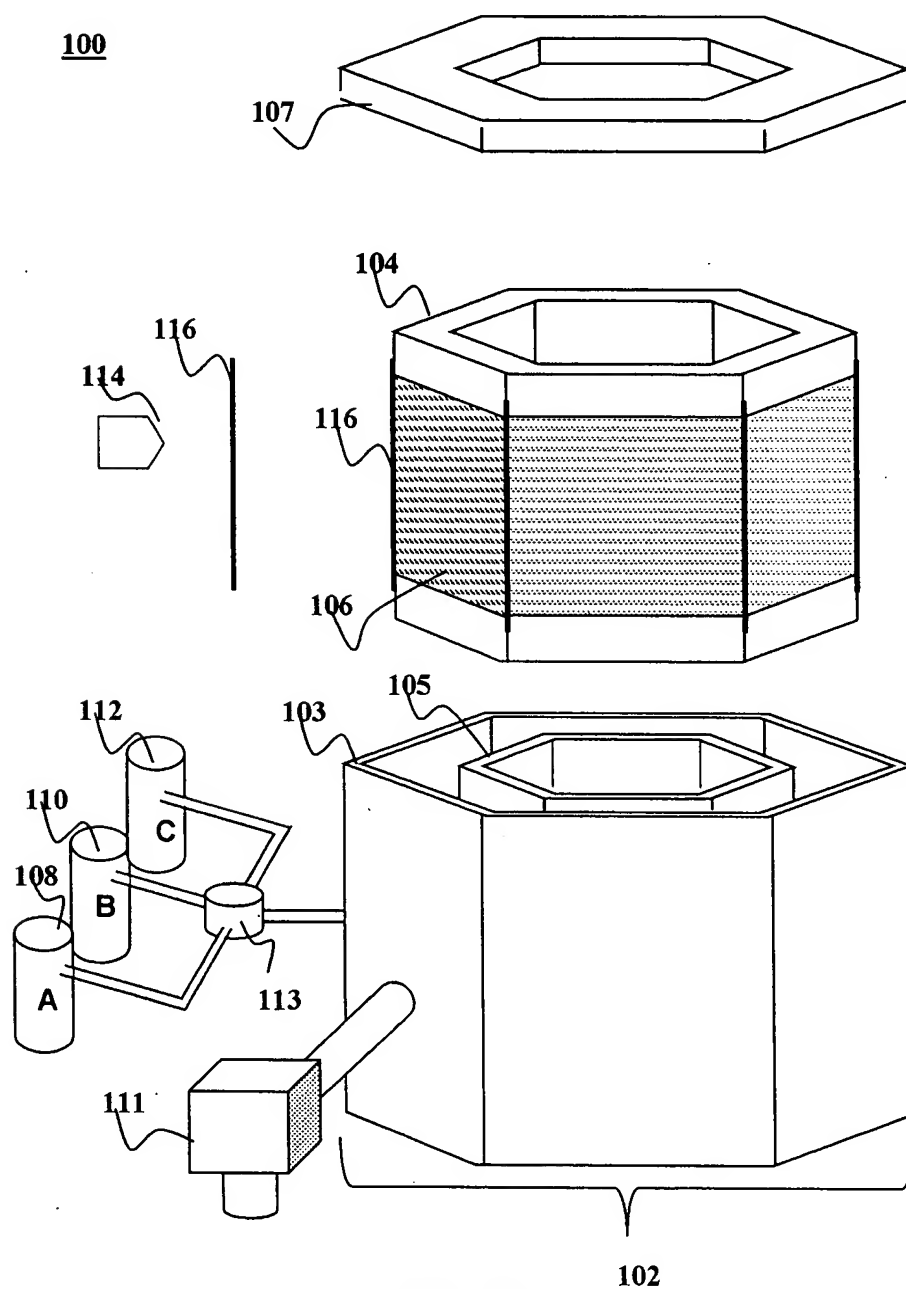
HIGH THROUGHPUT SURFACE TREATMENT ON COILED FLEXIBLE SUBSTRATES

ABSTRACT OF THE DISCLOSURE

- 5 One or more substrates may be coiled into one or more coils in such a way that adjacent turns of the coils do not touch one another. The one or more coiled substrates are placed in a treatment chamber where substantially an entire surface of the one or more coiled substrates may be treated with a surface treatment process. One or more spacers may be placed between adjacent layers of the coiled substrate before a full turn of the substrate has been
- 10 coiled around a carousel.

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"HIGH THROUGHPUT SURFACE TREATMENT ON COILED FLEXIBLE SUBSTRATES"

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FIG. 1B

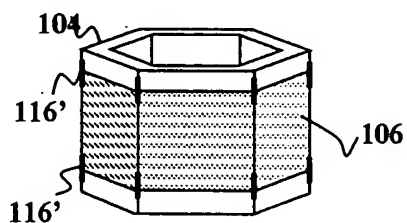


FIG 2A

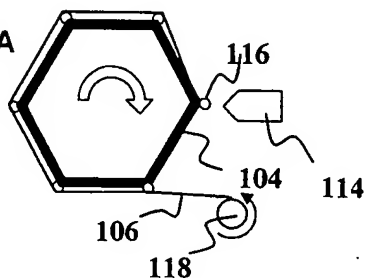


FIG 2E

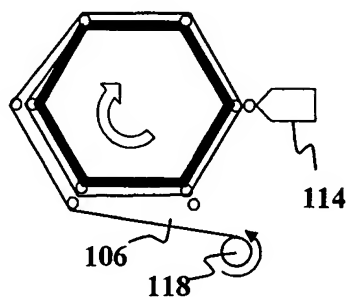


FIG 2B

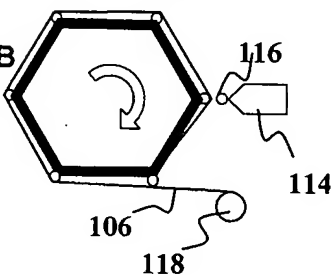


FIG 2F

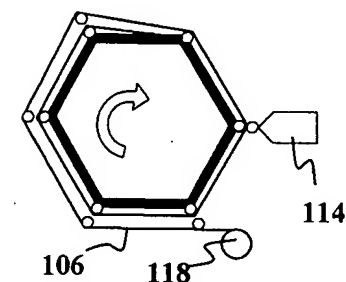


FIG 2C

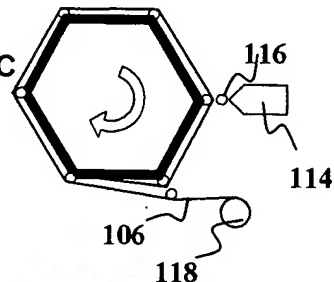


FIG 2G

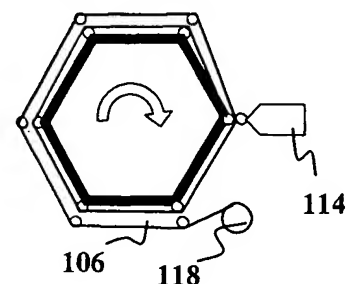


FIG 2D

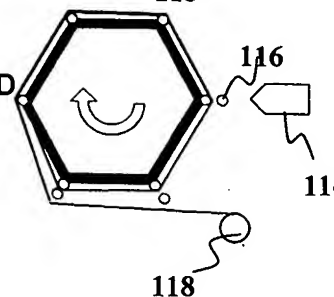
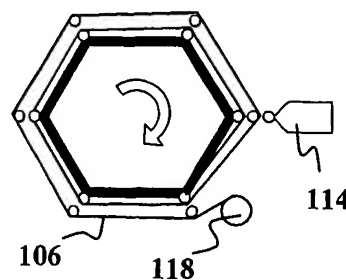


FIG 2H



"HIGH THROUGHPUT SURFACE TREATMENT ON COILED FLEXIBLE SUBSTRATES"

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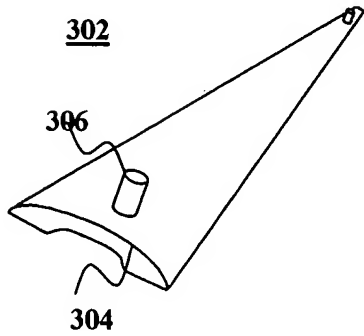


FIG 3A

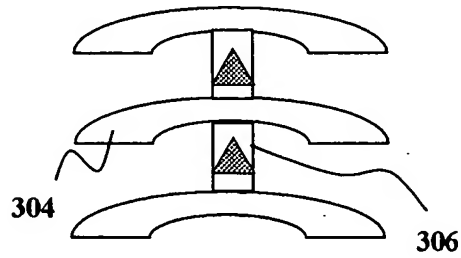


FIG 3B

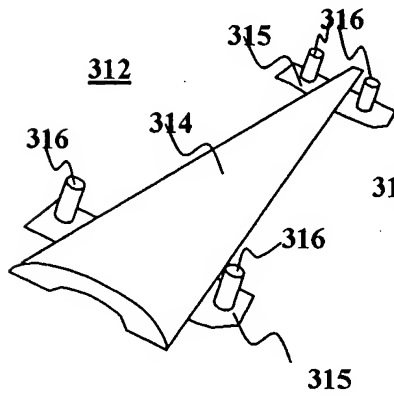


FIG 3C

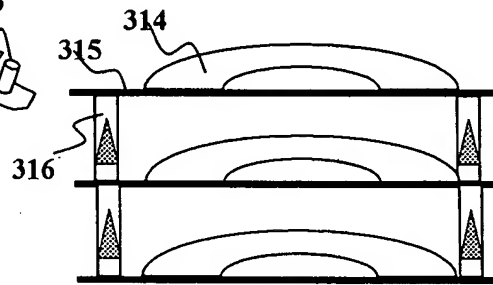
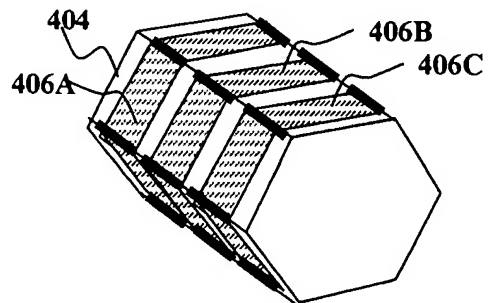


FIG 3D

FIG 4



"HIGH THROUGHPUT SURFACE TREATMENT ON COILED FLEXIBLE SUBSTRATES"

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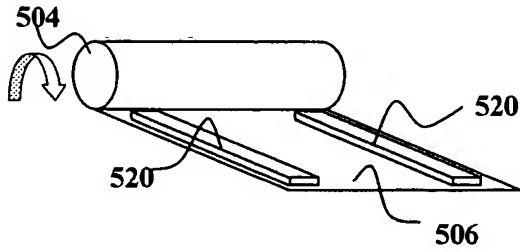


FIG. 5A

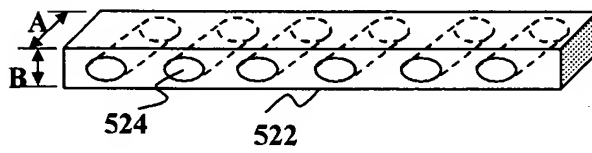


FIG. 5B

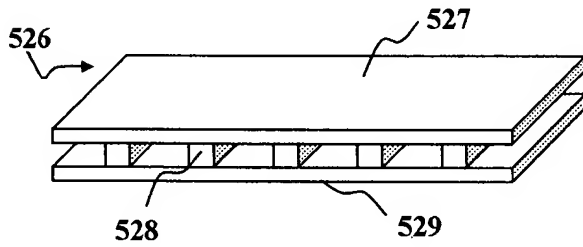


FIG. 5C

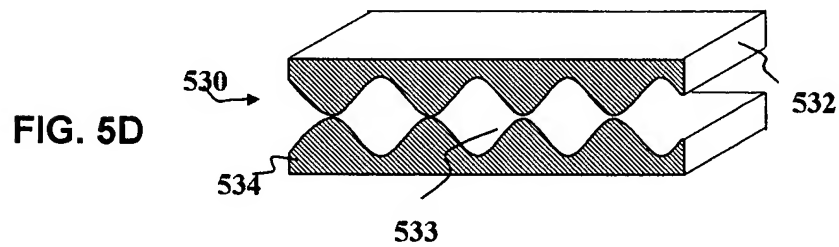


FIG. 5D

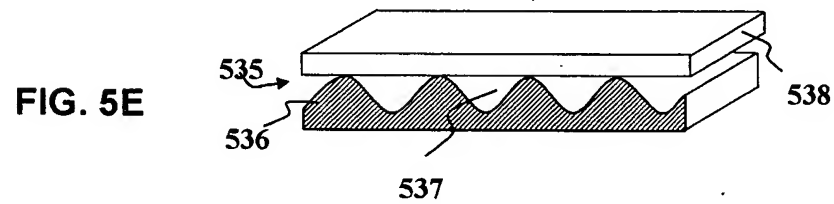


FIG. 5E

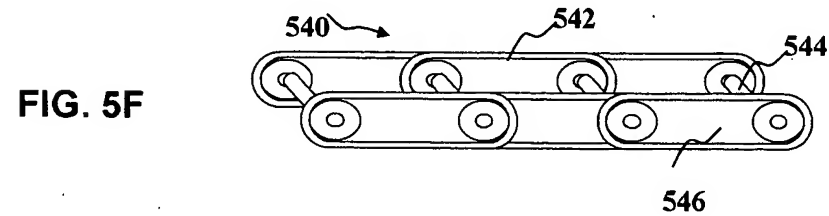


FIG. 5F

"HIGH THROUGHPUT SURFACE TREATMENT ON COILED FLEXIBLE SUBSTRATES

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FIG. 6A

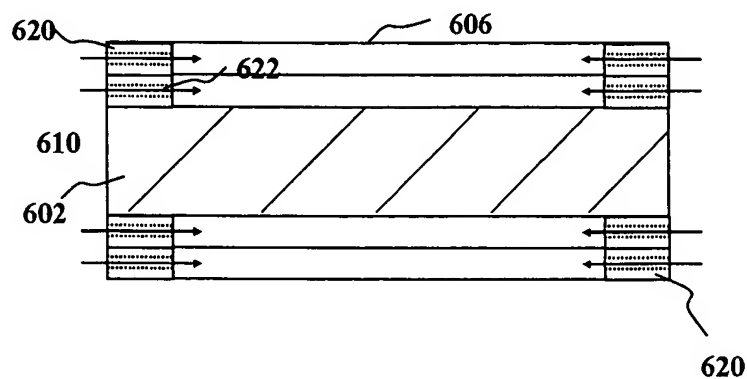


FIG. 6B

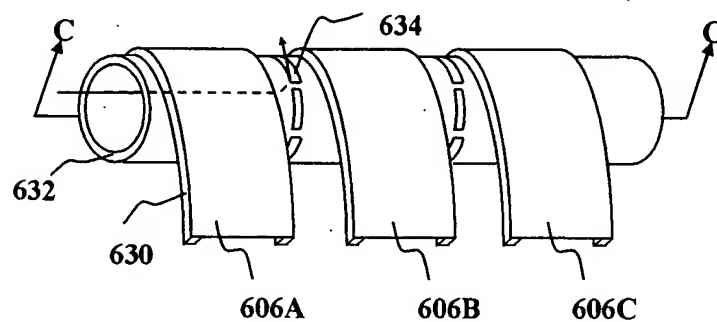
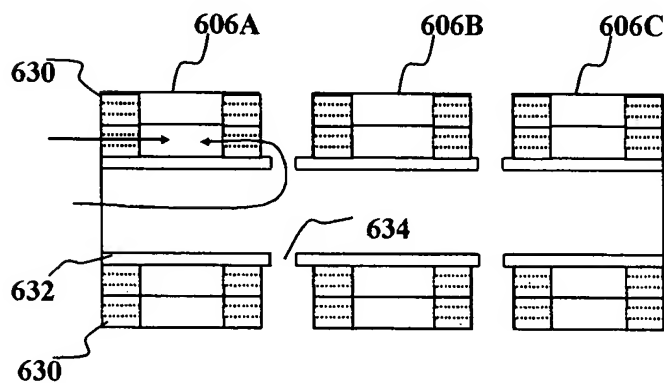


FIG. 6C



In the United States Patent and Trademark Office

Application No.: Not Yet Assigned
 Filed: Herewith
 Title: HIGH THROUGHPUT SURFACE TREATMENT ON COILED FLEXIBLE SUBSTRATES
 Applicant: Martin R. Roscheisen et al.
 Examiner: Not Yet Assigned
 Art Unit: Not Yet Assigned

Express Mail Label # EF084591344US

Mailed 2/19/2004
 Fremont, CA

Information Disclosure Statement

Commissioner of Patents and Trademarks
 Washington, District of Columbia 20231

Dear Sir or Madam:

Attached is a completed Form PTO-1449 and copies of the pertinent parts of the references cited thereon. It is requested that the document(s) on the enclosed form be made of record. As provided for by 37 CFR 1.97(g) and (h), no inference should be made that the information and references cited are prior art merely because they are in this statement and no representation is being made that a search has been conducted or that this statement encompasses all the possible relevant information.

It is requested that the document(s) on the enclosed form be made of record.

Part I (Authority)

This statement is filed pursuant to:

☒ 37 C.F.R. § 1.97(b).

This information disclosure statement is filed either (1) within three months of the filing date of the national applications; (2) within three months of the date of entry of the national stage as set forth in 37 C.F.R. § 1.491 in an international application; (3) before the mailing date of a first office action on the merits; or (4) before the mailing of a first Office action after the filing of a request for continued examination under § 1.114, whichever event occurs last.

Accordingly, this information disclosure statement requires no fee and no certification.

☐ 37 C.F.R. § 1.97(c).

This information disclosure statement is filed after the period specified in 37 C.F.R. § 1.97(b), but before the mailing date of either (1) a final action under 37 C.F.R. § 1.113 or (2) a notice of allowance under 37 C.F.R. § 1.311.

Accordingly, this information disclosure statement requires either the fee specified in 37 C.F.R. § 1.17(p) for submission of an information disclosure statement under 37 C.F.R. § 1.97(c) (\$180), or a certification according to 37 C.F.R. § 1.97(e).

☐ 37 C.F.R. § 1.97(d).

This information disclosure statement is filed after the period specified in 37 C.F.R. § 1.97(c). Accordingly, this information disclosure statement requires the petition fee specified in 37 C.F.R. § 1.17(p) to consider an information disclosure statement under 37 C.F.R. § 1.97(d) (\$180) and a certification according to 37 C.F.R. § 1.97(e).

Conditional Petition

It is respectfully requested that this information disclosure statement be considered, good cause being presented in Part III herein (certification). Please treat this paper as the required petition.

If this statement crosses in the mail with an office action, or is otherwise not in the indicated category of 37 C.F.R. § 1.97, it is respectfully requested that this statement be treated in the next appropriate category and made of record.

To the extent required, please treat this paper as a conditional petition for acceptance of the information disclosure statement.

Part II (Payment)

A check is enclosed as indicated:

- ☒ (X) No fee is due.
- ☐ () The fee specified in 37 C.F.R. § 1.17(p) for submission of an information disclosure statement under 37 C.F.R. § 1.97(c) is enclosed (\$180).
- ☐ () The petition fee specified in 37 C.F.R. § 1.17(p) to consider an information disclosure statement under 37 C.F.R. § 1.97(d) is enclosed (\$180).

Part III (Certification)

Pursuant to 37 C.F.R. § 1.97(e), I certify:

- ☒ (X) No certification is necessary.
- ☐ ()
 - (1) Each item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the statement.
 - ☐ () The "communication from a foreign patent office" referred to in the certification is an International Search Report, possibly issued by the U.S. Patent and Trademark Office in its capacity as an International Search Authority or International Preliminary Examining Authority.
 - ☐ () The "counterpart foreign application" referred to in the certification corresponds to an ancestor or descendent application of the application for which this information disclosure statement is filed.
- ☐ () (2) No item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, or, to my knowledge after making reasonable inquiry, was known to any individual designated in 37 C.F.R. § 1.56(c), more than three months prior to the filing of the statement.

Part IV (Additional Statement)

An additional statement regarding these items of information ☐ () is, ☒ (X) is not, enclosed.

Copies of the cited art reference A ☒ (X) is enclosed,

Copies of the cited art references _____ ☐ () are of record in parent application Serial No. _____ and will be provided if the Examiner deems it convenient.

Copies of the cited art references _____ ☐ () are not required under 37 CFR 1.98(a)(2)(i) because they are U.S. Patents and/or U.S. Patent Publications and

☐ () the present application was filed after June 30, 2003, or

☐ () the present application is an international application that entered the national stage under 35 USC 371 after June 30, 2003.

Dated: Feb. 19, 2004

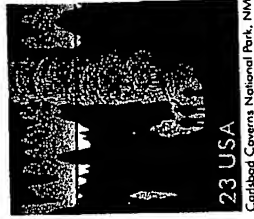
Respectfully submitted,



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FORM PTO-1449 U.S. DEPARTMENT OF COMMERCE				ATTY. DOCKET NO. NSL-025		SERIAL NO. Not Yet Assigned	
LIST OF PRIOR ART CITED BY APPLICANT (Use several sheets if necessary)				APPLICANT Martin R. Roscheisen et al.			
				FILING DATE Herewith		GROUP Not Yet Assigned	
U.S. PATENT DOCUMENTS							
EXAMINER INITIAL		DOCUMENT NUMBER	DATE	NAME	CLASS	SUBCLASS	FILING DATE IF APPROPRIATE
FOREIGN PATENT DOCUMENTS							
		DOCUMENT NUMBER	DATE	COUNTRY	CLASS	SUBCLASS	TRANSLATION
OTHER PRIOR ART (Including Author, Title, Date, Pertinent Pages, Etc.)							
	A	M.A. Cameron et al., "Atomic Layer Deposition of SiO ₂ and TiO ₂ in Alumina Tubular Membranes: Pore Reduction and Effect of Surface Species on Gas Transport" in <u>Langmuir</u> 2000, vol. 16, pp. 7345-7555, published on the web, 6/10/2000, American Chemical Society					
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JDI Patent
204 Castro Lane
Fremont, CA 94539



EXPRESS MAIL LABEL #: ET005599113US Docket No: NSL-024

Inventors Brian M. Sager

Title: "DEVICE BASED ON COATED NANOPOROUS STRUCTURE"

Received today:

Transmittal	Request for Non-publication	Title Page (1 page)
Specification: 14 Pages	Drawings: 2 Sheets	Declaration
Assignment	Power of Attorney by Assignee	3.73(b) Statement
Fee Transmittal	Credit Card Pmt Form (PTO-2038) for \$452	
IDS - PTO-1449	Copies of 11 references	